Premartensitic transition driven by magnetoelastic interaction in bcc ferromagnetic Ni_2MnGa

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We show that the magnetoelastic coupling between the magnetization and the amplitude of a short wavelength phonon enables the existence of a first order premartensitic transition from a bcc to a micromodulated phase in Ni_2MnGa. Such a magnetoelastic coupling has been experimentally evidenced by AC susceptibility and ultrasonic measurements under applied magnetic field. A latent heat around 9 J/mol has been measured using a highly sensitive calorimeter. This value is in very good agreement with the value predicted by a proposed model.

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Martensitic transitions (MT) are first order displacive structural phase transitions accompanied by a significant strain of the unit cell. In general, homogeneous and intracell (short-wavelength phonons) strains are necessary in order to describe the path followed by the atoms at the transformation. An interesting feature displayed by the systems undergoing this kind of first order transitions is the existence of precursor effects [1,2]. They reflect that, in a sense, the system prepares for the phase transition before it actually takes place. For instance, in *bcc* materials the $TA_2[110]$ phonon branch has low energy, the corresponding elastic constant (C') is very low and softening of all phonons and C' occurs on cooling [2].

The Ni_2MnGa Heusler alloy is investigated in the present work. At high temperature it is ferromagnetic (the Curie temperature is $T_c = 381$ K), displays a *bcc* structure with an $L2_1$ atomic order (space group $Fm3m$), and transforms martensitically at $T_M = 175$ K. This alloy is unique in the sense that (i) it is the only known bcc ferromagnetic material undergoing a MT and (ii) the MT is preceeded by a structural phase transition (intermediate transition) to a micromodulated phase (the cubic symmetry is preserved) resulting from the freezing of a $q = 0.33$ TA_2 phonon which becomes the intracell strain characterizing the new phase. Such a phase transition has been evidenced by neutron scattering [3], x-ray [4], electron microscopy [5],and ultrasonic measurements [6,7]. We have recently suggested that this transition to the premonitory (intermediate) phase is a consequence of the magnetoelastic interplay between the phonon and the magnetization [7]. At the MT the system transforms to a modulated structure with tetragonal symmetry (homogeneous strain) [8]. The modulation of the martensitic structure is different from that of the premartensitic phase. It has been argued [7] that the intermediate transition has to be first order because there is no complete softening of the frequency of the soft phonon; nevertheless, attempts in measuring a latent heat have not been successful [9] and a small thermal hysteresis has only been detected [10] in samples subjected to external stresses (which can result in a modification of the characteristics of the transition).

In this letter we present a phenomenological model for the intermediate transition based on a Landau expansion, which includes a magnetoelastic coupling. The primary order parameter is the amplitude η of a TA_2 [110] phonon, and secondary order parameters are: ε, a $(110)[1\bar{1}0]$ homogeneous shear suitable to describe a cubic to tetragonal change of symmetry, and M, the magnetization (considered here to be a scalar). In terms of these three order parameters we assume the free energy function to have the following general form:

$$\mathcal{F}(\eta,\varepsilon,M) = F_{str}(\eta,\varepsilon) + F_{mag}(M) + F_{me}(\eta,\varepsilon,M), \quad (1)$$

which includes a purely structural term F_{str}, a magnetic term F_{mag}, and a mixed term F_{me} accounting for the magnetoelastic interplay. Considering the symmetries of the system, the following expansions are proposed for the three contributions:

$$\begin{aligned} F_{str}(\eta,\varepsilon) &= \tfrac{1}{2}m^*\omega^2\eta^2 + \tfrac{1}{4}\beta\eta^4 + \tfrac{1}{6}\gamma\eta^6 + \tfrac{1}{2}c\varepsilon^2 \\ F_{mag}(M) &= -\tfrac{1}{2}AM^2 + \tfrac{1}{4}BM^4 \simeq A(M-M_0)^2 - \tfrac{1}{4}\tfrac{A^2}{B} \\ F_{me}(\eta,\varepsilon,M) &= \tfrac{1}{2}\kappa_1 M^2\eta^2 + \tfrac{1}{2}\kappa_2 M^2\varepsilon^2 \end{aligned}$$

All the coefficients in the above expansions are positive and only ω^2 is supposed to be temperature dependent [11]. Actually ω is identified as the frequency of the anomalous phonon which condensates at the intermediate transition. Experimentally, the square of this frequency has been shown to exhibit a marked linear decrease on approaching the intermediate transition [3]; hence we assume that: $m^*\omega^2 = a(T - T_u)$. We have not included any direct coupling between η and ε, which is supposed to be negligible in comparison with the magnetoelastic coupling. Concerning the purely magnetic contribution F_{mag}, considering that the intermediate phase appears well below the Curie point, the changes in the magnetization are expected to be small; therefore, it is reasonable to linearize F_{mag} around the value M_0 (the equilibrium magnetization close to the intermediate transition).

Minimization of $\mathcal{F}(\eta,\varepsilon,M)$ with respect to ε and M leads to an effective free energy function $\mathcal{F}_{eff}$ along a given transformation path ($\varepsilon = 0$ and $M = M_0/[1 + \frac{\kappa_1}{2A}\eta^2]$) in terms of the phonon amplitude η. Expanding

the term $[1+\frac{\kappa_1}{2A}\eta^2]^{-1}$ in power series and keeping only the terms up to sixth order, we obtain:

$$\mathcal{F}_{eff} = \frac{1}{2}m^*\widetilde{\omega}^2\eta^2 + \frac{1}{4}\widetilde{\beta}\eta^4 + \frac{1}{6}\widetilde{\gamma}\eta^6 \qquad (2)$$

where: $m^*\widetilde{\omega}^2 = m^*\omega^2 + \kappa_1 M_0^2 = a(T - [T_u - \frac{\kappa_1 M_0^2}{a}]) = a(T - T_0)$; $\widetilde{\beta} = \beta - \frac{\kappa_1^2 M_0^2}{A}$, and $\widetilde{\gamma} = \gamma + \frac{3}{4}\frac{\kappa_1^3 M_0^2}{A^2}$.

The interesting point to be stressed is: provided that $\frac{\kappa_1^2 M_0^2}{A}$ is large enough, $\widetilde{\beta}$ can become negative, and in this case a first order transition can take place before the system becomes linearly unstable at $T_0 (= T_u - \frac{\kappa_1 M_0^2}{a})$. It is also worth noting that, in case there was not magnetoelastic coupling, only a continuous transition at $T = T_u$ would be possible. In general, a first order transition is predicted by the Landau theory when the system symmetries enable the existence of a cubic invariant in the free energy expansion. However, in our case the possibility of the first order character for the premartensitic transition is a consequence of the non-linear coupling between the symmetry-breaking order parameter and the magnetization. There is some experimental evidence that this transition has a first order character. The main argument supporting this point is the fact that the frequency of the anomalous phonon does not reach zero value at any temperature [3]. Actually, ω^2 decreases linearly with temperature and reaches a minimum (finite) value at the transition temperature. Extrapolation down to $\omega = 0$ predicts that a complete phonon softening would occur 5 K below the actual first order transition. Based on this experimental evidence, in the following we will assume that in Ni_2MnGa the premartensitic transition is first order, that is, $\widetilde{\beta} < 0$.

The equilibrium first order transition temperature T_I is obtained from the two conditions: $\partial\mathcal{F}_{eff}/\partial\eta = 0$ and $\mathcal{F}_{eff}(\eta_I) = \mathcal{F}_{eff}(\eta = 0)$, where $\eta_I = \pm(-3\widetilde{\beta}/4\widetilde{\gamma})^{\frac{1}{2}}$ is the value of the order parameter of the distorted phase at the transition temperature. These conditions lead to a transition temperature $T_I = \frac{3}{16a}\frac{\widetilde{\beta}^2}{\widetilde{\gamma}} + T_0$, higher than T_0. The corresponding entropy change at T_I is obtained from:

$$\Delta S = \left(\frac{\partial \mathcal{F}_{eff}}{\partial T}\right)_0 - \left(\frac{\partial \mathcal{F}_{eff}}{\partial T}\right)_{\eta_I} = -\frac{1}{2}a\eta_I^2 = \frac{3a\widetilde{\beta}}{8\widetilde{\gamma}} \qquad (3)$$

rendering a transition latent heat: $L = T_I\Delta S$. It has been reported that no latent heat has been detected using differential scanning calorimetric techniques [9]. Nevertheless, a heat capacity anomaly (jump) has recently been observed at the premartensitic transition [7]. Such a jump can be calculated from our Landau model as:

$$\frac{\Delta C}{T_I} = \left[\frac{\partial \Delta S}{\partial T}\right]_{T=T_I} = -\frac{1}{2}a\left(\frac{\partial \eta^2}{\partial T}\right)_{T=T_I} = -\frac{a^2}{\widetilde{\beta}} \qquad (4)$$

From (3) and (4) and using the expression of T_I, a latent heat $L = 2\,(T_0 - T_I)\,\Delta C$ is obtained. T_0, T_I and ΔC have been measured experimentally, thus enabling an evaluation of the latent heat. Taking $T_0 = 225$ K, $T_I = 230$ K and $\Delta C \simeq 0.7$ J/mol K, the values $L \simeq -7$ J/mol and $\Delta S \simeq -0.03$ J/mol K are obtained. These values are quite small (for comparison note that at the MT the latent heat L is around 100 J/mol and $\Delta S \simeq 0.5$ J/mol K).

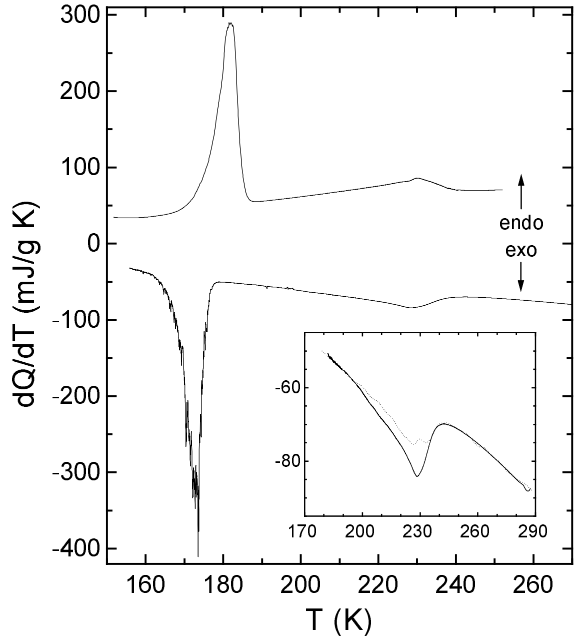

FIG. 1. Thermograms recorded during cooling and heating calorimetric runs in a Ni_2MnGa sample. The small peak corresponds to the premartensitic transition and the large one to the martensitic transition. The inset shows the premartensitic peak with the measured base line for evaluation of the latent heat.

In order to corroborate the validity of the values predicted by the model, calorimetric measurements have been carried out using a highly sensitive scanning microcalorimeter [12]. This special calorimeter enabled the use of large samples (this is not usual in standard differential scanning calorimeters which are designed to operate with very small samples of a few mg). A single crystal of Ni_2MnGa of 2.9 g of mass and a Cu reference with the same mass have been used. An example of the measured thermogram is shown in Fig. 1. The large thermal effect corresponds to the MT. This transition has a jerky character which is especially remarkable in the exothermic forward transition. Also an intense acoustic emission has been detected during this MT [13]. A very small peak is clearly observed above the MT. It corresponds to the premartensitic transition. The dots shown in the inset below the peak correspond to a measurement of the difference in the specific heats of a smaller sample of the same crystal [14] and a Cu reference, carried out using a modulated differential scanning calorimeter. This measurement determines the base line that enables a correct integration of the calorimetric peak leading to the transition latent heat. We have obtained $L = -9 \pm 3$ J/mol. This value is in very good agreement with our numerical

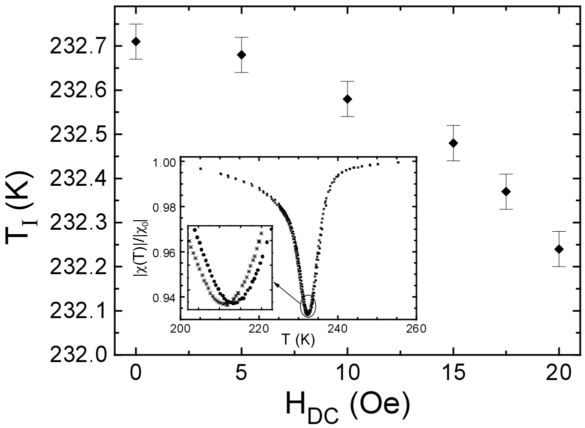

FIG. 2. Transition temperature as a function of a DC magnetic field applied along the [100] direction. The inset shows an example of the AC magnetic susceptibility χ across the transition, for two different applied fields (0 (dots) and 20 Oe (stars)). Data are normalized by the measured value at 260 K (χ_0). Measurements have been conducted with an AC field of 2 Oe and a frequency of 666 Hz .

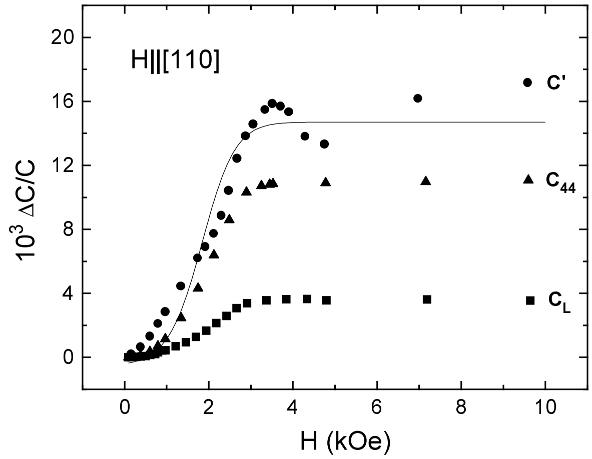

FIG. 3. Relative change of the elastic constants (solid symbols) as a function of an applied magnetic field H along the [110] direcion. The solid line corresponds to C' computed from measured values of C_{11},C_{44} and C_L.

prediction based on the Landau model.

For a first order transition, the Clausius-Clapeyron law must hold. In the present investigation, the magnetoelastic interaction must lead to a change in the transition temperature (T_I) under application of a magnetic field. We have checked the field dependence of T_I by measuring the magnetic susceptibility accross the intermediate transition with different DC fields applied along the [100] direction, using an AC susceptometer. Results are shown in Fig. 2. An unambiguous decrease in T_I with increasing magnetic field has been found. The change in T_I becomes more pronounced at larger values of the field. Such a nonlinear behaviour seems to be due to a decrease in ΔS as the field increases; this decrease would be consistent with the fact that with the application of magnetic field, the transition temperature approaches the unstability value. Moreover, the observed decrease is in concordance with the behaviour obtained by computing dT/dH from the model.

The elastic constant C' corresponding to a $(110)[1\bar{1}0]$ shear can also be obtained from the model as $C' = c + \kappa_2 M^2$. With the aim of providing experimental evidence for this magnetoelastic effect we have measured the elastic constants under application of a magnetic field at room temperature (ferromagnetic state) by the use of ultrasonic techniques. These experiments will be reported in full elsewhere [13]. In Fig. 3 we show an example of the behaviour exhibited by the three independent elastic constants for a cubic symmetry. In all cases, prior to each measurement, the sample was heated up to a temperature well above the Curie point and cooled down to room temperature so that each ultrasonic measurent corresponds to the first magnetization process. The ultrasonic waves associated with C' were affected by a strong scattering by the magnetic domains. This resulted in a larger error in the determination of the field dependence of C'. For this reason, we also measured C_{11}, which enabled to compute C' as $C_{11} + C_{44} - C_L$; the result is shown as a continuous line in Fig. 3. We have found that all elastic constants increase with the magnetic field up to a saturation value [15]. For the same range of magnetic fields, an increase of the magnetization from zero to a saturation value has been reported in a similar sample [16]; this indicates that the change in the elastic constants presented here is associated to a change in the value of the magnetization.

Across the intermediate phase transition, M undergoes a change (we recall that M depends on η), which results in a jump of C' at the transition, $\Delta C' = \kappa_2(M_I^2 - M_0^2)$, where M_I is the magnetization in the $\eta \neq 0$ modulated phase. Since $M_I < M_0$, it is expected that $\Delta C' < 0$. It is worth noting that this is in agreement with measurements of the temperature dependence of C' which show a marked decrease of this elastic constant at the premartensitic transition [6,7].

The model presented in this letter accounts for the magnetoelastic interplay between the structural order parameters and the magnetization. Since in the temperature range of interest Ni_2MnGa shows soft magnetic properties, this interplay is mostly related to the reorientation of the magnetic moments. The interaction between the magnetic and structural degrees of freedom has been demonstrated by the measured field dependence of C' and of the intermediate transition temperature. The coupling between the amplitude of the anomalous short-wavelength phonon (primary order parameter) and the magnetization gives the possibility for the occurrence of a first order transition before a linear phonon unstability is reached. The thermodynamic quantities of this transition have been obtained from the model. They are in good agreement with experimental results. Actually,

a predicted latent heat of around -7 J/mol is in excellent agreement with the value obtained from calorimetric measurements. The intermediate transition takes place at a temperature slightly above the one where the anomalous transverse phonon would become unstable. This indicates that the first order character of this transition is weak, in concordance with the small value found for the latent heat.

The microscopic origin of the phonon anomaly and magnetoelastic coupling related to this phase transition are not explained by the proposed phenomenological model. It has been suggested [17] that their origin lies in the electron-phonon coupling and specific nesting properties of the multiply connected Fermi surfaces. While this explains similar short-wavelength phonon anomalies observed in Ni-Al alloys [18], no specific calculations in such a direction have, to our knowledge, been performed in the case of the system studied here. Nevertheless, no premartensitic transition has been reported to occur in Ni-Al. Actually, the ferromagnetic character of the Ni_2MnGa is the main difference between these two alloys.

The MT in non-ferromagnetic alloys have been described using Landau-type models. In these models, the transition takes place as a consequence of the anharmonic coupling between an anomalous transverse phonon and an homogeneous strain [19]. Such a coupling ($\eta^2\varepsilon$) is not included in our model. However, we argue that the magnetoelastic interaction indirectly couples η and ε. At the MT, ε (tetragonal distortion) becomes different from zero and the periodicity of the transverse modulation with wave vector $\zeta = 0.33$ is modified (a five layer modulation is obtained). To account for such a modification in the periodicity, an explicit wavevector dependence of the free energy should be included in the Landau model. It is also worth noticing that reorientation of martensitic twin variants has been achieved recently by the application of magnetic field [16].

In conclusion we have presented a model that accounts for the first order phase transition between the *bcc* and the intermediate phases. The first order character has been experimentally demonstrated by the measurement of a latent heat and by the magnetic field dependence of the transition temperature. In the model, the first order transition occurs as a consequence of a magnetoelastic coupling. Such a coupling has also been experimentally evidenced. Hence, the premartensitic transition must be considered as a magnetically driving precursor effect announcing the MT by the modification of the dynamical response of the *bcc* parent lattice. Within a general framework, the results presented here evidence that coupling of a secondary field (magnetic in this case) to incipient unstable excitations, associated to structural degrees of freedom, can fundamentally affect the characteristics of a phase transition.

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